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(54) Title: SURFACE COATING OF POLYMER OBJECTS

(57) Abstract

A method of modifying surfaces of polymeric objects which comprises immersing the polymeric object in an aqueous dispersion of a polymerizable surfactant, a cross-linking agent, and a free radical initiator and exposing the immersant to ultraviolet light to form a permanent, cross-linked surface coating on the object. Also disclosed are coated objects prepared by this method, which is particularly suited for coating contact lenses.

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SURFACE COATING OF POLYMER OBJECTS

BACKGROUND OF THE INVENTION

The present invention is directed to modifying the surfaces of solid materials and more particularly to the use of polymerizable surfactants for such modifications.

Surface structure and composition determine many of the physical properties and ultimate uses of solid materials. Characteristics such as wetting, friction, electrostatic charging, and adhesion are largely influenced by surface characteristics. Of particular concern are the effects of such surface characteristics on biocompatibility. The alteration of surface characteristics is therefore of special significance in biotechnical applications. Improved methods are accordingly sought for modifying solid surfaces, particularly the surfaces of polymeric objects.

Random, grafted, polymerized surfactants have been used to modify the surfaces of hydrophobic polymers by the adsorption of the surfactant onto the surfaces of polymeric objects from an aqueous dispersion. Lee, J. H., Interactions of PEO-Containing Polymeric Surfactants With Hydrophobic Surfaces, The University of Utah (1988)(hereinafter "Lee"). Lee--particularly concerned with reducing the absorption of blood plasma proteins on hydrophobic surfaces--teaches the synthesis of polymeric surfactants by random free radical copolymerization of a hydrophobic methacrylate (hexyl methacrylate or lauryl methacrylate), a hydrophilic methacrylate (polyethylene oxide methacrylate), and methyl methacrylate.

Akashi, M., et al., "Graft Copolymers Having Hydrophobic Backbone and Hydrophilic Branches. IV. A Copolymerization Study of Water-Soluble Oligovinylpyrrolidone Macromonomers," J. Polymer Sci.: Part A: Polymer Chemistry, Vol. 27, pp. 3521-3530 (1989)(hereinafter "Akashi") teaches amphiphiles prepared by random free radical copolymerization of carboxyl group-terminated oligovinylpyrrodidone with methyl methacrylate or styrene. Syntheses of vinylphenyl-terminated and methacryloyl-terminated oligovinylpyrrolidone macromonomers are described.

Polymerizable surfactants have been used to modify the properties of polymers in aqueous solution. For example, Schulz, et al., "Copolymers of Acrylamide and Surfactant Macromonomers: Synthesis and Solution Properties," Polymer, Vol. 28, pp. 2110-2115 (Nov., 1987)(hereinafter "Schulz") describes macromonomer surfactants wherein the surfactant character is achieved by the addition of a small hydrophobic functionality (e.g., nonylphenol) to a water-soluble polyethylene oxide chain. Related materials and methods are disclosed in U.S. Patent 4,075,411.

Polymerizable surfactants have also been used to modify the surface properties of solids. One class of materials used for this purpose are lipids (non-polymeric materials) which are rendered polymerizable by the addition of various functionalities such as methacrylate groups [Ringsdorf, H., et al., "Hydrophilic Spacer Groups in Polymerizable Lipids: Formation of Biomembrane Models form Bulk Polymerized Lipids," J. Am. Chem. Soc., Vol. 107, pp. 4134-4141 (1985)] and various vinyl groups [Ringsdorf, H., et al., "Saturated and Polymerizable Amphiphiles with Fluorocarbon Chains. Investigation in Monolayers and

Liposomes," J. Am. Chem. Soc., Vol. 106, pp. 7687-7692 (1984)]. These polymerizable lipid surfactants have been used to prepare liposomes used in the formation and stabilization of biomembrane models (often referred to as polymeric liposomes).

Polyfunctional polymerizable surfactants have also been used in coatings to modify the surface properties of polymeric objects. European Patent Publication No. 153,133 (hereinafter "Regen"). Preferred polymerizable surfactants taught by Regen are polyfunctional lipids. Regen teaches that monofunctional polymerizable surfactants are ineffective for modifying surfaces of polymeric objects. Other polyfunctional polymerizable surfactants are disclosed in U.S. Patent No. 3,541,138.

An object of Regen was to overcome the limitations of Langmuir-Blodgett processes, especially when applied to more complex surface topographies. Polymerizable surfactants have of course been employed in Langmuir-Blodgett films. These multilayer surfactant assemblies are exploited in microlithography and other opto-electronic systems. Fendler, J.H., "Polymerized Monolayers from a Styrene Functionalized Surfactant," Colloids and Surfaces, Vol. 35, pp. 343-351 (1989).

Contact lenses are conventionally produced by one of three general techniques--lathing, static casting, and spin casting. Combinations are also known. For example, semi-finished buttons (having one final lens surface) may be formed by static or spin casting and the second lens surface may be produced by lathing. Static and spin casting have the advantage of producing lenses with fewer processing steps than lathing. In either of the molding techniques, the anterior and posterior surfaces of the lens may be formed in one

step. Static casting does this by providing two mold surfaces; spin casting does this by providing a mold surface to form the anterior surface and by using the forces generated by spinning liquid monomer to form the posterior surface.

One of the challenges faced when producing lenses by molding is achieving release of the lenses from the molds without damaging the lens surfaces. The phenomenon of lens adherence is a consequence of chemical interactions between mold surfaces and monomer mixtures during polymerization. Among the proposals to meet this challenge is U.S. Patent 4,534,916, which teaches adding (nonpolymerizable) surfactants to the monomer mix. The surfactant addition is reported to improve the surface quality of lenses by decreasing the number of surface defects resulting from mold release (especially of xerogel lenses).

The '916 patent seeks improved surface quality by reducing lens damage during demolding. Others have sought to improve surface quality more directly--by surface modifications. For example, U.S. 4,546,123 teaches covalent attachment of (nonpolymerizable) surfactant molecules to a hydrogel lens surface.

The macromonomer technique for preparing graft copolymers of controlled architecture is well known. Macromonomers or macromers are polymers of molecular weight ranging from the hundreds to tens of thousands, with one of the end groups functionalized to enter into further polymerization. Milkovich, Chiang and Schultz demonstrated the synthesis and applications of a variety of macromers. R. Milkovich, M.T. Chiang, U.S. Patent No. 3,842,050 (1974); Schultz, G.O. and Milkovich, R., J. App. Polym. Sci., 27, 4773 (1982);

Schultz, G. O. & Milkovich, R., J. Polym. Sci. Polym. Chem. Ed., 22, 1633 (1984).

Yamashita, Y.; "Synthesis and Application of Fluorine Containing Graftcopolymers," Polymer Bull., 5, 335-340 (1981); "Synthesis and Characterization of Functional Graft Copolymers by Macromonomer Technique", J. Appl. Polym. Sci., 36, 193-199 (1981); "Synthesis of N-Hydroxyethyl-N-Methylmethacrylamide and Its Use in the Macromonomer Synthesis", J. Polym. Sci., Polym. Letters Ed., 19, 629-636 (1981); (hereinafter "Yamashita") teaches a method of making macromers and the use of macromers to make graft copolymers. Yamashita used free radical polymerization in the presence of an effective chain transfer agent which controlled the molecular weight of the final macromer and also provided a functional end group. Thioglycolic acid, for example, is an effective chain transfer agent which provides a carboxylic acid functional end group. The end group can subsequently be reacted with, e.g., glycidyl methacrylate to give a terminal methacrylate polymerizable group. Yamashita used macromers of MMA to prepare graft copolymers of fluoroalkyl acrylates with polyMMA grafts. Yamashita does not teach the synthesis of polymerizable surfactants by the macromonomer technique.

SUMMARY OF THE INVENTION

It has now been found that the surface properties of a polymeric object may be modified by immersing the object in an aqueous dispersion of a polymerizable surfactant, a cross-linking agent, and a free radical initiator and exposing the immersion to ultraviolet light to form a permanent, cross-linked surface coating on the object. The present invention provides greater

versatility as compared to those processes using only polyfunctional polymerizable surfactants. While any polymerizable surfactant may be employed, a preferred class of polymerizable surfactants are novel surface active macromonomers described by the formula:

$$DC[A_xB_y]$$

wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional chain transfer agent, D is an ethylenically unsaturated end group, y is within the range from about 0.1 to about 0.9, and x + y = 1.

DETAILED DESCRIPTION OF THE INVENTION

Notations such as "(meth)acrylate" or "(meth)acrylamide" are used herein to denote optional methyl substitution. Thus, methyl (meth)acrylate includes both methyl acrylate and methyl methacrylate, and N-alkyl (meth)acrylamide includes both N-alkyl acrylamide and N-alkyl methacrylamide.

Polymerizable surfactants useful in the practice of this invention include any of the many polymerizable surfactants known to those skilled in the art. Examples of such surfactants include: monofluoroalkyl esters of alkendioic acids, 2-(meth)acrylamido-2-alkylethane-1-sulfonic acid; α,ω-(meth)acrylamidoalkanoic acid; dimethylhexadecyl[11-(methacryloyloxy)undecyl]ammonium halide; dimethylhexadecyl[11-(methacryloyloxy)undecyl]ammonium dimethyl phosphate; 1-palmitoyl-2-[11-(methacryloyloxy)undecyl]-*sn*-glycero-3-phosphocholine; 1,2-bis[11-(methacryloyloxy)undecyl]-*sn*-glycero-3-phosphocholine; 1,2-bis(heptadeca-10,12-diynoyl)-*sn*-glycero-3-phosphocholine; 1,2-bis(heneicosa-10,12-

diynoyl)-*sn*-glycero-3-phosphocholine; 1,2-bis(hexacosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine; bis[10-(methacryloyloxy)decyl] hydrogen phosphate; bis[11-(methacryloyloxy)undecyl]dimethylammonium halide; and bis[11-(methacryloyloxy)undecyl]dimethylammonium dimethyl phosphate.

Particularly preferred polymerizable surfactants useful in the process of this invention are surface active macromonomers described by the formula:

$$DC[A_xB_y]$$

wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional chain transfer agent, D is an ethylenically unsaturated end group, y is within the range of about 0.1 to about 0.9, and $x + y = 1$.

Suitable ethylenically unsaturated hydrophilic monomers ("A" in the above formula) include ethylenically unsaturated polyoxyalkylenes, polyacrylamides, polyvinylpyrrolidones, polyvinyl alcohols, poly (hydroxyethyl methacrylate) or poly (HEMA), and N-alkyl-N-vinyl acetamides. Ethylenic unsaturation may be provided by (meth)acrylate, (meth)acrylamide, styrenyl, alkenyl, vinyl carbonate and vinyl carbamate groups. Preferred hydrophilic macromonomers include methoxypolyoxyethylene methacrylates of molecular weights from 200 to 10,000, more preferred are methoxypolyoxyethylene methacrylates of molecular weight range of 200 to 5,000 and most preferred are methoxypolyoxyethylene methacrylates of molecular weight range of 400 to 5,000. Additional preferred hydrophilic macromonomers include poly-N-vinylpyrrolidone methacrylates of molecular weights of 500 to 10,000. More preferred are poly-N-

vinylpyrrolidone methacrylates of molecular weights of 500 to 5,000 and most preferred are poly-N-vinylpyrrolidone methacrylates of molecular weights of 1000 to 5,000. Other preferred hydrophilic macromonomers include poly-N,N-dimethyl acrylamide methacrylates of molecular weights of 500 to 10,000. More preferred are poly-N,N-dimethyl acrylamide methacrylates of molecular weights of 500 to 5,000 and most preferred are poly-N,N-dimethyl acrylamide methacrylates of molecular weights of 1000 to 5,000.

Suitable ethylenically unsaturated hydrophobic monomers ("B" in the above formula) include alkyl (meth)acrylates, N-alkyl (meth)acrylamides, alkyl vinylcarbonates, alkyl vinylcarbamates, fluoroalkyl (meth)acrylates, N-fluoroalkyl (meth)acrylamides, N-fluoroalkyl vinylcarbonates, N-fluoroalkyl vinylcarbamates, silicone-containing (meth)acrylates, (meth)acrylamides, vinyl carbonates, vinyl carbamates, styrenic monomers [selected from the group consisting of styrene, alpha-methyl styrene, para-methyl styrene, para-t-butyl monochloro styrene, and para-t-butyl dichloro styrene] and polyoxypropylene (meth)acrylates. Preferred hydrophobic monomers include methyl methacrylate, dodecyl methacrylate, octafluoropentyl methacrylate, perfluorooctyl methacrylate, methacryoyl oxypropyl tris(trimethylsiloxy)silane (TRIS).

The functional chain transfer agent ("C" in the above formula) controls the molecular weight of the copolymer and provides appropriate functionality for subsequent addition of a polymerizable group. Suitable functional chain transfer agents include mercapto carboxylic acids, mercapto alcohols (also known as hydroxymercaptans), and aminomercaptans. Preferred chain transfer agents include thioglycolic acid, 2-

mercaptoethanol and 2-aminoethane thiol. The molar ratio of chain transfer agent to total monomer used in the copolymerization is preferably about 0.01 to about 3, more preferably about 0.02 to about 2, and still more preferably about 0.05 to about 1.

Selection of the ethylenically unsaturated end group ("D" in the above formula) is determined by the functional group of the functional chain transfer agent. For example, if the chain transfer agent contains a carboxylic acid group, glycidyl methacrylate can provide a methacrylate end group. If the chain transfer agent contains hydroxy or amino functionality, isocyanato ethyl methacrylate or (meth)acryloyl chloride can provide a methacrylate end group and vinyl chloro formate can provide a vinyl end group. Other combinations will be apparent to those skilled in the art.

Varying the ratio of hydrophilic monomer to hydrophobic monomer changes the surface properties of polymeric objects made from the surface active macromers. For example, when preparing contact lenses containing certain surface active macromers of this invention, it has been found that higher amounts of hydrophilic component optimized mold release characteristics of the lenses but that optimum clinical performance was obtained with a relatively lower amount of hydrophilic component. Accordingly, the selection of a particular ratio will be governed by the particular surface properties ultimately sought for the polymeric object. Generally, however, y is preferably in the range from about 0.1 to about 0.9, more preferably in the range from about 0.3 to about 0.9, and still more preferably in the range from about 0.5 to about 0.8.

The random copolymers, from which the surface-active macromers are derived, are prepared by copolymerizing at least one ethylenically unsaturated hydrophobic monomer and at least one ethylenically unsaturated hydrophilic monomer in the presence of a functional chain transfer agent. The random copolymers are formed by a free radical mechanism using a wide variety of known free radical catalysts such as the diacyl peroxides (e.g., benzoyl peroxide); dialkyl peroxides (e.g., di-tert-butyl peroxides); ketone peroxides (e.g., methylethyl ketone peroxide); and peresters which readily hydrolyze (e.g., tert-butyl peracetate, tert-butyl perbenzoate, di-tert-butyl diperphthalate). A particularly useful class of peroxy initiators are the organic hydroperoxides such as cumene hydroperoxide, methylethyl ketone hydroperoxide, tert-butyl hydroperoxide, etc. The initiators should be used at a concentration of about 0.01 to about 10% by weight of the total formulation, preferably about 0.1 to about 5%. Another class of initiators comprises carbonyl-containing ultraviolet-activated free radical generators, such as acetophenone, benzophenone, and benzoin ethers. Other suitable UV initiators and initiator mixtures will be apparent to one of ordinary skill in the art. Solvents can be used in the process. Solvent choice will depend upon the solubility parameters of the comonomers used and should be chosen to allow full solubilization of all polymerizate components. Preferred solvents include tetrahydrofuran, dioxane, chloroform, dicloromethane, methanol and mixtures of these solvents.

The crosslinking agent employed in the coating method of this invention must be hydrophobic. The purpose of this invention is to render a hydrophobic

polymer surface hydrophilic. The use of a hydrophobic crosslinking agent insures maximum coverage of such surface. In addition, the solubilization of a hydrophobic crosslinking agent by the polymerizable surfactant in aqueous solution provides a more intimate mixture of the surfactant and crosslinking agent and, thereby, a more effective surface coating.

Suitable crosslinking agents for this invention are hydrophobic molecules having two or more polymerizable groups. The polymerizable groups will be ethylenically unsaturated. The ethylenic unsaturation may be provided by (meth)acrylate, (meth)acrylamide, styrenyl, vinyl or other alkenyl functionality. Examples of suitable crosslinking agents include: allyl methacrylate, ethylene glycol dimethacrylate, divinyl ethylene urea, neopentyl glycol dimethacrylate, divinyl benzene and 1,3-bis(4-methacryloxybutyl)tetramethyl siloxane.

The polymeric coating of this invention is formed by a free radical mechanism using a wide variety of known free radical catalysts such as the diacyl peroxides (e.g., benzoyl peroxide); dialkyl peroxides (e.g., di-tert, -butyl peroxides); ketone peroxides (e.g., methylethyl ketone peroxide); and peresters which readily hydrolyze (e.g., tert-butyl peracetate, tert-butyl perbenzoate, di-tert-butyl diperphthalate). A particularly useful class of peroxy initiators are the organic hydroperoxides such as cumene hydroperoxide, methylethyl ketone hydroperoxide, tert-butyl hydroperoxide, etc. The initiators should be used at a concentration of about 0.01 to about 10% by weight of the total formulation, preferably about 0.1 to about 5%. Another class of initiators comprises carbonyl-containing ultraviolet-activated free radical

generators, such as acetophenone, benzophenone, and benzoin ethers. Other suitable UV initiators and initiator mixtures will be apparent to one of ordinary skill in the art.

Surface coatings of this invention are applied to a polymeric object by immersing the object in an aqueous dispersion of polymerizable surfactant, crosslinking agent, and free radical initiator and exposing the immersion to ultraviolet light. The concentration of polymerizable surfactant in the aqueous dispersion is preferably in excess of the surfactant's critical micelle concentration, CMC. The CMC is the concentration at which the surfactant molecules begin to associate into aggregates in solution [M. J. Rosen, "Surfactants and Interfacial Phenomena", Wiley-Interscience: New York, 1989, p. 109]. Generally that molar concentration is in the range of about 0.1 to about 10^{-4}. The crosslinker concentration in the aqueous dispersion will typically be in the range of about 1 to about 10^{-4} parts by weight. The free radical initiator concentration in the aqueous dispersion will typically be in the range of about 0.1 to 10^{-4} parts by weight.

The polymeric objects whose surfaces may be modified by these techniques include polymers having a wide variety of compositions and shapes. Polymeric objects of particular concern in the development of this invention were contact lenses and the particular surface modification sought was to increase surface wettability without sacrificing otherwise beneficial bulk properties of the polymeric material (especially oxygen permeability). Although the utility of the macromonomers of this invention will be further illustrated by referring particularly to their

incorporation into contact lenses, it will be understood that the utility of the macromonomers of this invention is not so limited.

One class of contact lenses whose surface may be usefully modified by the macromonomers of this invention are soft hydrogel lenses. Conventional monomer systems for such lenses employ a hydrophilic monoolefinic monomer (i.e., a monoethylenically unsaturated monomer) and a polyolefinic (usually diolefinic) monomer (e.g., a polyethylenically unsaturated compound which functions as a cross-linking agent) in an amount sufficient to insolubilize the resulting hydrophilic hydrogel but insufficient to destroy the hydrophilic properties. Mixtures of hydrophilic monoolefinic monomers are used as well as mixtures of cross-linking agents. Other monomers which are copolymerizable with the hydrophilic monomer are also used to adjust various properties of the polymeric material, as is well known in the art.

Illustrative hydrophilic monomers include water soluble monoesters of (meth)acrylic acid with an alcohol having an esterifiable hydroxyl group and at least one additional hydroxyl group such as the mono- and poly-alkylene glycol monoesters of (meth)acrylic acid, e.g., ethylene glycol mono(meth)acrylate, diethylene glycol mono(meth)acrylate, propylene glycol mono(meth)acrylate, dipropylene glycol mono(meth)acrylate, and the like; the N-alkyl and N,N-dialkyl substituted (meth)acrylamides such as N-methyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, and the like; N-vinylpyrrolidone and the alkyl substituted N-vinyl pyrrolidones; glycidyl (meth)acrylates; the unsaturated amines; the alkoxy ethyl acrylates; mixtures thereof; and others known to the art.

Illustrative di- or higher polyfunctional species employed as cross-linking agents are divinylbenzene, ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, and the (meth)acrylate esters of polyols such as triethanolamine, glycerol, pentaerythritol, butylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, mannitol, and sorbitol. Further illustrations include N,N-methylene-bis-(meth)acrylamide, sulfonated divinylbenzene, and divinylsulfone.

Illustrative of other copolymerizable monomers are hydrophobic (meth)acrylic esters such as alkyl (meth)acrylates wherein the alkyl moiety contains 1-5 carbon atoms.

While soft, hydrophilic, gel-type lenses may be modified by the macromonomers of this invention, of greater interest is the modification of lenses prepared from a formulation including at least one silicone monomer and at least one hydrophilic monomer. Included in this class of materials are soft contact lens formulations (both hydrogel and nonhydrogel) and rigid gas permeable contact lens formulations.

Preferred soft hydrogel formulations are those described in U.S. Patent Application Serial Nos. 07/363,662 filed June 7, 1989 and 07/364,204 filed May 2, 1989, the entire contents of which are incorporated herein by reference. Other examples of useable formulations are found in U.S. Patent Nos. 4,136,250; 4,740,533; 4,711,943; 4,189,546; and 4,153,641.

One type of presently preferred hydrogel formulations incorporate prepolymers of the general formula:

$$E(*D*A*D*G)_a*D*A*D*E' \text{ or}$$
$$E(*D*G*D*A)_a*D*G*D*E'$$

where

A denotes a divalent polymeric radical represented by the general formula chosen from the group of

$$(CH_2)_{1-4}\left(\begin{array}{c} R^S \\ | \\ Si-O \\ | \\ R^S \end{array}\right)_p \begin{array}{c} R^S \\ | \\ Si-(CH_2)_{1-4} \\ | \\ R^S \end{array}$$

wherein R^S denotes an alkyl radical or a short chain fluorinated alkyl radical with 1 to 3 carbon atoms; and

p provides a moiety weight of 400 to 10,000;

D denotes an alkyl diradical, an alkyl cycloalkyl diradical, a cycloalkyl diradical, an alkylaryl diradical or an aryl diradical, with 6 to 30 carbon atoms;

G denotes an alkyl diradical, a cycloalkyl diradical, an alkyl cycloalkyl diradical, an aromatic diradical or an alkylaromatic diradical with 1 to 40 carbon atoms which may have ether, thio, or amine linkages in the main chain;

* denotes a urethane or ureido linkage; and

E and E' denote polymerizable unsaturated organic radicals represented by the general chemical formula

$$R^3CH=\overset{R^2}{\overset{|}{C}}(CH_2)_w(X)_x(Z)_z(Ar)_y-R^1-$$

wherein R^1 denotes a divalent alkylene radical with 1 to 10 carbon atoms;

R^2 denotes a -H or $-CH_3$ radical;

R^3 denotes a -H radical or an alkyl radical with 1 to 6 carbon atoms or a $-\overset{O}{\overset{\|}{C}}Y-R^4$ radical where Y is -O-, -S- or -NH- and R^4 denotes an alkyl radical with 1 to 12 carbon atoms;

X denotes $-\overset{O}{\overset{\|}{C}}-$, or $-O-\overset{O}{\overset{\|}{C}}-$;

Z denotes -O-, -S-, or -NH-;

Ar denotes an aromatic radical with 6 to 30 carbon atoms;

a is at least 1;

w is 0 to 6;

x is 0 or 1;

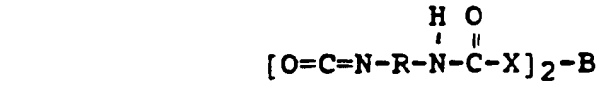
y is 0 or 1; and

z is 0 or 1.

The isocyanates which can be used in preparation of these urethane prepolymers include toluene diisocyanate, 4,4'-diphenyl diisocyanate, 4,4'-diphenylene methane diisocyanate, p-phenylene diisocyanate, dianisidine diisocyanate, 1,5 napthalene diisocyanate, 4,4'-diphenyl ether diisocyanate, 4,4'(dicyclohexyl)methane diisocyanate, 1,3-bis-(isocyanato methyl)cyclohexane, cyclohexane diisocyanato, tetrachlorophenylene diisocyanate, isophorone diisocyanate, and 3,5-diethyl-4,4'-diisocyanato diphenyl methane.

Other diisocyanates which may be used are higher molecular weight diisocyanate formed by reacting polyamines which are terminally capped with primary or secondary amines, or polyhydric alcohols with excess of any of the above described diisocyanates. In general,

these high molecular weight diisocyanates will have the general formula



wherein R is a divalent organic radical with 2 to about 20 carbon atoms, X is -O-, or -NR'-, where R is -H or a lower alkyl, and B is a divalent organic radical.

The diisocyanate is reacted with low molecular weight diols or glycols such as 2,2-(4,4' dihydroxydiphenyl)-propane (bisphenol-A), 4,4'-isopropylidine dicyclohexanol (hydrogenated biphenol-A), ethoxylated bisphenol-A, propoxylated bisphenol-A, 2,2-(4,4'-dihydroxydiphenyl)-pentane, α,α'-(4,4'-dihydroxydiphenyl)-p-diisopropyl benzene, 1,3 cyclohexane diol, 1,4-cyclohexane diol-1,4-cyclohexane dimethanol, bicyclic and tricyclic diols such as 4,8-bis-(hydroxymethyl)-tricyclo [5.2.1.$0^{2,6}$] decane, neopentyl glycol, 1, 4 butanediol, 1,3-propanediol, 1,5-pentanediol, diethylene glycol, triethylene glycol and the like.

These hard segments form hard domains in the final polymer or copolymer by association via hydrogen bonding with other rigid segments. The degree of association within the hard domain can be modified by controlling the amount of hydrogen bonding between the segments by either 1) decreasing the overall weight content of the hard segment in the prepolymer by increasing the molecular weight of the soft segment or 2) by decreasing the amount of hydrogen bonding density in the hard segment by either using relatively soft, longer chained diols, or by using primary amines or secondary amines capped low molecular weight compounds

in conjunction with the diisocyanates rather than the diols.

The hard segments are then reacted with a relatively high molecular weight polymer which is α,ω-endcapped with two active hydrogens, usually hydroxyl groups. These segments form the so-called soft segment of the prepolymer. Various types of high molecular weight polymers can be used including in general polymers of the following formulae

a) $HO\ (CH_2)\ (R^PO)_n\ (CH_2)\ OH$;

b) $HO\ (CH_2)\ (R^PO)_m\ (CH_2)\ OH$; and

c) $$HO\ (CH_2)_{1-4}\left(\begin{array}{c} R^S \\ | \\ Si\text{-}O \\ | \\ R^S \end{array}\right)_m \begin{array}{c} R^S \\ | \\ Si \\ | \\ R^S \end{array} - (CH_2)_{1-4}\ OH$$

Formulae a) represents polyoxyalkyleneglycols. These diols include polymers prepared from the epoxides: ethylene oxide 1,2-propylene oxide, 1,2-butylene oxide, 2,2 epoxydecane, 1,2-epoxyoctane, 2,3-epoxy norborane, 1,2-epoxy-3-ethoxy propane, 2,2-epoxy-3-phenoxypropane, 2,3-epoxypropyl-4-methoxy phenyl ether, tetrahydrofluran, 1,2-epoxy-3-cyclohexyloxy propane, oxetane, 1,2-epoxy-5-hexene, 1,2-epoxyethylbenzene, 1,2-epoxy-1-methoxy-2-methylpropane, benzyloxy propylene oxide, the like and combinations thereof.

The preferred polymers of this class are polypropylene glycols of molecular weights, 2000, 3000 and 4000 and more and polyoxyethylene polyoxypropylene block copolymers with molecular weight greater than 2000.

Formulae b) represents polyfluoroethers with α,ω- active hydrogens. This class of polymers can be synthesized as taught in U.S. Patent No. 3,810,874. Generally, these polymers should have molecular weights between 400 and 10,000.

Formulae c) represents α,ω- dihydroxyl alkyl endblocked polysiloxane which for the purpose of the present invention should have a molecular weight in the range of 400 to 10,000. These polysiloxanes can be synthesized by reacting a disiloxane of the general formula

$$HO\ (CH_2)_{1-4}\ \begin{matrix} CH_3 & CH_3 \\ | & | \\ Si-O-Si \\ | & | \\ CH_3 & CH_3 \end{matrix}\ (CH_2)_{1-4}\ OH$$

with cyclopolydimethyl siloxane under acidic conditions.

Alternately, the disiloxane can be replaced with dimethoxydimethylsilane or diethoxy dimethyl silane to produce the α,ω- dihydroxy endcapped polysiloxanes.

The endcapping monomers used in the prepolymer are generally represented by the formula

$$R^3CH=\overset{R^2}{\overset{|}{C}}\ (CH_2)_w\ (X)_x\ (Z)_z\ (Ar)_y\ -R^1-$$

as defined supra. The Stage B reaction product is reacted with an excess of suitable acrylate or methacrylate esters containing a hydroxy or amine group on the non-acrylate or non-methacrylate portion of the monomer to form the endcaps of the above formula. Suitable endcap monomers include hydroxyethyl acrylate,

hydroxyethyl methacrylate, aminoethyl methacrylate, 3 hydroxypropyl methacrylate, amino propyl methacrylate, hydroxyhexylacrylate, t-butylaminoethyl methacrylate, monoacrylate or monomethacrylate esters of bisphenol-A and/or bisphenol-B.

The urethane prepolymers are formed by two general synthetic approaches. One approach produces the hard-soft-hard prepolymer while the second approach produces the soft-hard-soft prepolymer.

The scheme used to produce hard-soft-hard urethane prepolymer employed three stages. In the first stage (STAGE A) 2 mole equivalents of diisocyanate are reacted with about 1 mole equivalent low molecular weight diols. If these diols are represented by the symbol ♦G♦, where ♦ denotes a hydroxyl radical and G represents the rest of the diol compound, and the diisocyanate functional compound is represented by •D• where • represents an isocyanate radical, the STAGE A reaction can be schematically represented as follows:

$$2\bullet D\bullet + \blacklozenge G\blacklozenge \longrightarrow \bullet D*G*D\bullet$$

where * denotes a urethane or a ureido linkage. STAGE A produces a so-called "Hard" segment. As is known to those skilled in polymer chemistry, the product •D*G*D• is the mathematical average of all reaction product molecules. The reaction product of the actual reaction will contain •O• and $\bullet D(*G*D)_c*G*D$ with $c \geq 2$. Again, the formulas are numerical averages.

STAGE B involves reacting about one half mole equivalent of a α,ω- diol endcapped long chain polymer with the reaction product of STAGE A. If ♦A♦ represents the long chain diol the STAGE B Reaction is

$$2\bullet D*G*D\bullet + \blacklozenge A\blacklozenge \longrightarrow [\bullet D*G*D*]_2A$$

In STAGE C, the reaction product from STAGE B is reached with a molar excess of an endcapping monomer which has: 1) hydroxyl or amine functionality; and 2) some polymerizable unsaturation. If the endcapper is represented by the symbol E♦, where ♦ is -OH or $-NH_2$ or -NH-, the reaction proceeds generally as

$$[\bullet D*G*D*]_2A + 2E\blacklozenge \longrightarrow [E*D*G*D*]_2A$$

Optionally, STAGE B can be run with molar excess of ♦A♦ to produce multiblock polymers of the general formula $\bullet(D*G*D*A)_a*D*G*D\bullet$ where a is at least 1. This reaction product would be endcapped in STAGE C above.

The second general synthetic scheme using the same nomenclature described is represented by the following general formulae:

STAGE A

$$2 \bullet D \bullet + \blacklozenge A\blacklozenge \longrightarrow [\bullet D*]_2A$$

STAGE B

$$2[\bullet D*]_2A + \blacklozenge G\blacklozenge \longrightarrow [\bullet D*A*D*]_2G$$

STAGE C

$$[\bullet D*A*D*]_2G + 2E\blacklozenge \longrightarrow [E*D*A*D*]_2G$$

In general, each of the reaction stages is run until the reactive step is complete. Reaction progress in STAGES A and B reactants can be monitored by acid base

titration. The isocyanate content was calculated by the difference of acid equivalents between a stock solution dibutylamine and its reaction product with the diisocyanate reaction intermediate. The reaction was also monitored by ATR-IR for the appearance/disappearance of peaks at 1700 cm^{-1}, which indicated the presence of

-C-, and 2250 cm^{-1} which indicated consumption of -N=C=O.

The synthesis of the prepolymer may be run neat or in solution. A wide range of aprotic solvents can be used to synthesize the prepolymers of the present invention. Solvents useful in the synthesis include toluene, methylene, chloride, benzene, cyclohexane, hexane, heptane and the like. Preferred solvents are toluene, methylene chloride and mixtures thereof.

Reaction of the prepolymer precursors may be accomplished in the presence or absence of catalysts for urethane reactions, such catalysts being well known in the art. The first step of prepolymer synthesis where diisocyanate is first reacted with a short carbon chain (2 to 30 carbon atoms) diol, particularly where an aromatic diisocyanate is used, proceeds very rapidly, even in the absence of any catalyst. In fact, during the step of reacting diisocyanate and short chain diol, temperature control may be required in order to avoid/minimize side reactions.

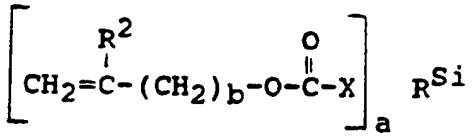
Preferably, the first step of prepolymer synthesis in accordance with the present invention is carried out below about 100°C, most suitably within the range of from about 60°C to about 90°C. Thereafter, the second step of the reaction is carried out at comparable

temperatures, preferably within the range of from about 40°C to 70°C. The final step of prepolymer formation suitably is effected at temperatures of from about room temperature to about 100°C, with a narrow range of from about 40°C to about 50°C being most preferred. As will be apparent to those skilled in the art, optimal reaction conditions, such as temperatures and duration, are selected for each individual reaction system to achieve conditions that produce a favorable rate of reaction without fostering undesirable side reactions.

Among the suitable catalysts for use in prepolymer formation are tin salts and organic tin esters, such as dibutyl tin dilaurate, tertiary amines, such as triethyl diamine and other recognized catalysts, such as 1,4-diaza (2.2.2)-bicyclooctane (DABCO).

These silicone-containing prepolymers may be copolymerized with a wide variety of hydrophilic monomers to produce soft hydrogel contact lenses. Hydrophilic monomers suitable for this use include 2-hydroxyethylmethacrylate, N-vinyl pyrrolidone, (meth)acrylamide, vinyl acetamide, and other ethylenically unsaturated hydrophilic monomers. Further comonomers may also be added to enhance wetting or to modify other properties as is generally known to those skilled in the art.

Another presently preferred hydrogel formulation incorporates silicone-containing vinyl carbonate or vinyl carbamate prepolymers of the general formula:



wherein X denotes an -O-, -S-, or $-NR^3-$ divalent radical;

R^{Si} denotes a silicone containing organic radical;

R^2 denotes -H or $-CH_3$;

A is 1, 2, 3, or 4; and

b is 0 or 1.

Suitable silicone-containing organic radicals (R^{Si}) include the following:

$$-(CH_2)n\left[Si\ (CH_2)_mCH_3\right]_3;$$

$$-(CH_2)n\ Si(OSi\left[(CH_2)_mCH_3\right]_3)_3;$$

$$-(CH_2)_n\begin{bmatrix}R^1\\Si-O\\R^1\end{bmatrix}_d R^{Cl};\ \text{and}$$

$$-(CH_2)_n\begin{bmatrix}R^1\\Si-O\\R^1\end{bmatrix}_d\begin{matrix}R^1\\-Si-R^{Cl}\\R^1\end{matrix}$$

where R^1 denotes a monovalent organic radical such an an alkyl radical with 1 to 6 carbon atoms, or a fluoroalkyl radical with 1 to 6 carbon atoms;

R^{Cl} denotes

$$-(CH_2)_p-O-C-CH=CH_2$$

p is 1 to 6; and

d is 1-200, and

where n is 1, 2, 3, or 4, and m is 0, 1, 2, 3, 4, or 5.

The silicone-containing vinyl carbonate/carbamate monomers specifically include 3-[tris(trimethylsiloxy)silyl]propyl vinyl carbonate; 1,3-bis[4-(vinyloxycarbonyloxy)but-1-yl]tetramethyl-disiloxane; 3-(trimethylsilyl)propyl vinyl carbonate;

t-butyldimethylsiloxyethyl vinyl carbonate; trimethyl-silylmethyl vinyl carbonate; trimethylsilylethyl vinyl carbonate; 2,2,2-trifluoroethyl vinyl carbonate; t-butyl vinyl carbonate; 3-[tris(trimethylsiloxy)silyl] propyl vinyl carbonate; 2,2,2-trifluoroethyl vinyl carbamate; 1,1,1,3,3,3-hexafluoro-2-propyl vinyl carbonate; 3-(vinyloxycarbonylthio)propyl-[tris(trimethylsiloxy)silane]; 3-[tris-(trimethylsiloxy)silyl]propyl vinyl carbamate; "V_2D_{25}", 2,2,2-trifluoro-1-phenylethyl vinyl carbonate; 1-adamantane vinyl carbonate, 1-adamantanethyl vinyl carbonate, 1-adamantaneethyl vinyl carbonate; and 1-adamantane vinyl carbamate.

Preferred nonhydrogel soft contact lens formulations are mixtures of polymerizable polysiloxanes containing fluorinated side chains and internal wetting agents. Further components such as toughening agents, crosslinking agents, and other auxiliary modifiers are desirably present as taught in U.S. Patent 4,810,764, the entire content of which is incorporated herein by reference.

Polymerizable, fluorinated polysiloxanes employed in this embodiment of the invention are described by the general formula:

$$A(CH_2)_4-\left[\begin{array}{c}R^1\\ |\\ Si-O\\ |\\ R^2\end{array}\right]_m-\left[\begin{array}{c}R^3\\ |\\ Si-O\\ |\\ R^4\end{array}\right]_n-\begin{array}{c}R^1\\ |\\ Si\\ |\\ R^2\end{array}-(CH_2)_4-A$$

where A denotes an activated unsaturated group, $-R^1$ and R^2 independently denote alkyl radicals with 1 to 6 carbon atoms or phenyl radicals; R^3 and R^4

independently denote alkyl radicals with 1 to 6 carbon atoms, phenyl radicals, or fluorinated alkyl radicals with 1 to 6 carbon atoms, provided that at least one of R^3 or R^4 is a fluorinated alkyl radical with 1 to 6 carbon atoms; m + n is at least 1; and n is at least 1.

Internal wetting agents ("hydrophilic monomers") useful in this embodiment of the invention include N-alkyenoyl trialkylsilyl aminates (hereinafter "NATA") (described in U.S. Patent No. 4,652,622) represented by the general formula

$$CH_2=C(E)C(O)N(H)CH(G)(CH_2)_mC(O)OSi(R)_3$$

wherein

E is H or CH_3,

G is $(CH_2)_xC(O)OSi(R)_3$ or H,

R is CH_3, C_2H_5 or C_3H_7,

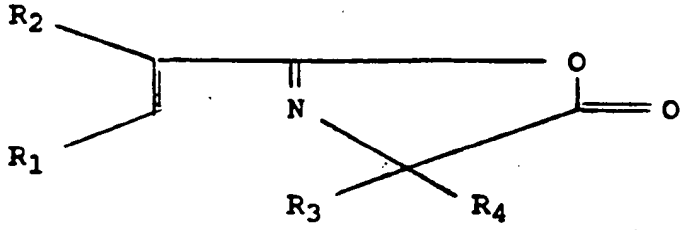
m is an integer from 1 to 15,

x is an integer from 1 to 10, and

m + x is an integer from 1 to 15

Acryloyl- and methacryloyl-, mono- and dicarboxylic amino acids, hereinafter NAA, impart desirable surface wetting characteristics to polysiloxane polymers, but precipitate out of siloxane monomer mixtures before polymerization is completed. NAA can be modified to form trialkylsilyl esters which are more readily incorporated into polysilocane polymers. The preferred NATA's are trimethylsilyl-N-methacryloylglutamate, triethylsilyl-N-methacryloylglutamate, trimethyl-N-methacryloyl-6-aminohexanoate, trimethylsilyl-N-methacryloyl-aminododecanoate, and bis-trimethylsilyl-N-methacryloyl aspartate.

The preferred internal wetting agents are oxazolones of the general formula



where

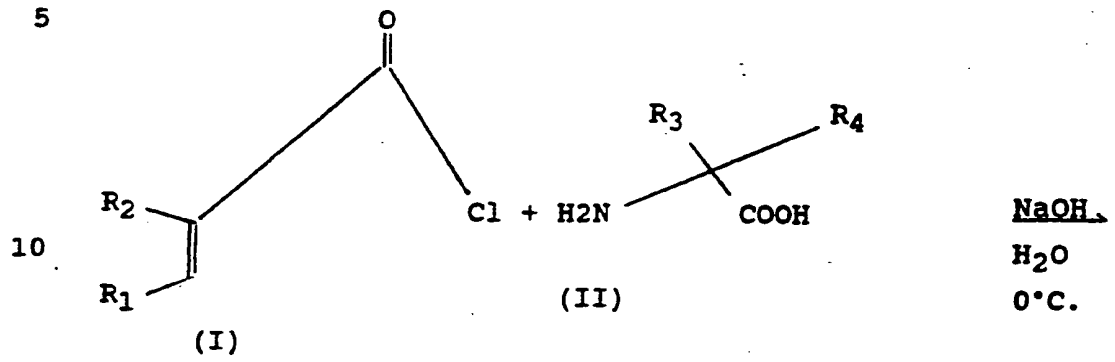
R_1 and R_2 independently denote H or CH_3; and

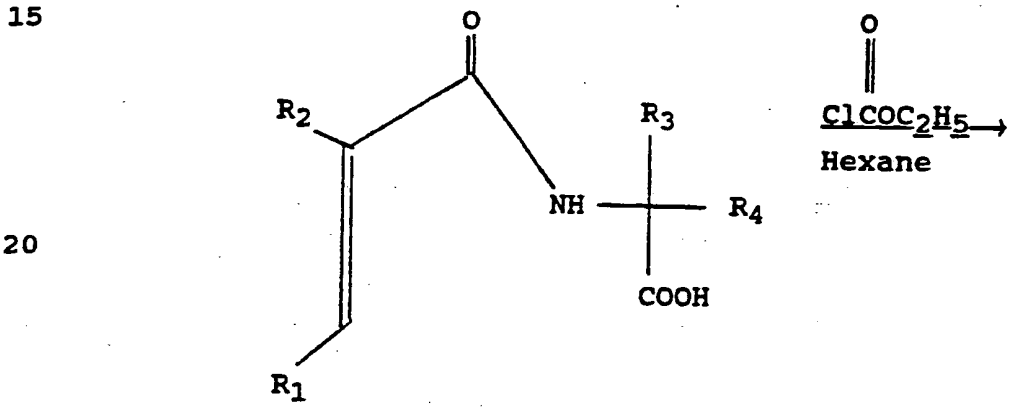
R_3 and R_4 independently denote methyl or cyclohexylradicals.

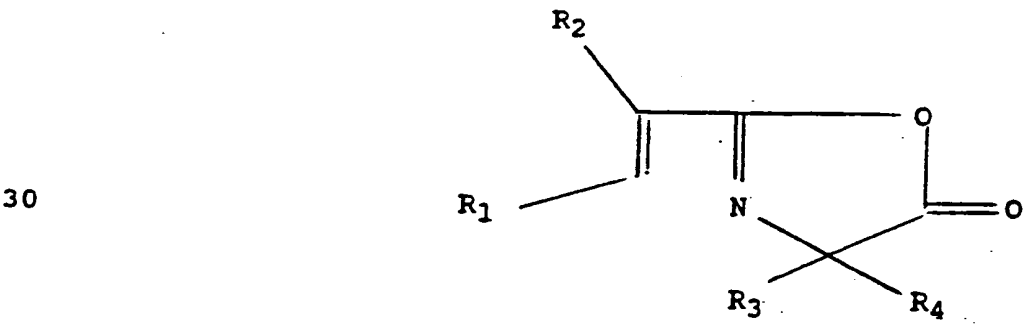
These preferred internal wetting agents specifically include 2-isopropenyl-4,4-dimethyl-2-oxazolin-5-one (IPDMO), 2-vinyl-4,4-dimethyl-2-oxazolin-5-one (VDMO), cyclohexane spiro-4'-(2'isopropenyl-2'-oxazol-5'-one) (IPCO), cyclohexane-spiro-4'-(2'-vinyl-2'-oxazol-5'-one) (VCO), and 2-(-1-propenyl)-4,4-dimethyl-oxazol-5-one (PDMO).

These preferred internal wetting agents have two important features which make them particularly desirable wetting agents: (1) They are relatively non-polar and are compatible with the hydrophobic monomers (the polysiloxanes and the toughening agents), and (2) They are converted to highly polar amino acids on mild hydrolysis, which impart substantial wetting characteristics. When polymerized in the presence of the other components, a copolymer is formed. These internal wetting agents result through the carbon-carbon double bond with the endcaps of the polysiloxane monomers, and with the toughening agents to form copolymeric materials particularly useful in biomedical devices, especially contact lenses.

These oxazolones are prepared by the general reaction sequence







The first step being a Shotten-Bauman acrylation of an amino acid. Upon completion of this step the

polymerizable functionality is introduced by using either acryloyl or methacryloyl chloride.

Rigid gas permeable contact lens formulations which are suitable for the practice of this invention are silicone-based copolymers prepared from siloxanylalkyl esters of methacrylic acid and other acrylate, methacrylate, or itaconate monomers in many known formulations. See U.S. Patent Nos. 4,424,328; 4,463,149; 4,664,479; and 4,686,267.

This invention is further described by the following Examples which are intended to be illustrative, not limiting.

EXAMPLES

EXAMPLE 1

Polymerization of 1-Vinyl-2-pyrrolidinone

Distilled 1-vinyl-2-pyrrolidinone, (NVP) 40 g, 2-mercaptoethanol, 2.80 g and azobisisobutyronitrile (AIBN, recrystallized from ethanol) 0.59 g were combined with 100 mL of anhydrous tetrahydrofuran (THF) in a 250 mL three neck flask. The flask was also fitted with a mechanical stirrer and a reflux condenser. A slow stream of nitrogen was used to deoxygenate the solution for 15 minutes. After 24 hours of reflux under a nitrogen atmosphere, no vinyl protons could be detected in the 60 Mhz NMR spectra (6.5-7.0 ppm). The hydroxy-terminated polymer was precipitated from 2 L of anhydrous ethyl ether. The solid was dissolved in 200 ml of THF and the precipitation repeated twice. The white solid, 29.37 g (69% yield), was dried under reduced pressure.

EXAMPLE 2

Synthesis of a Polyvinyl Pyrrolidinone (PVP) Macromer

Hydroxy-terminated PVP, 9.0 g (from Example 1), was dissolved in 90 mL of chloroform, in a 250 mL 3-neck flask fitted with a magnetic stirrer, a reflux condenser, and an addition funnel. Dibutyltin dilaurate, 32.5 mg, and butylated hydroxy toluene, 2.1 mg (BHT), were added. Isocyanatoethyl methacrylate, 0.86 g (ICEM) in 10 mL $CHCl_3$, was added dropwise. Following the addition the solution was heated to reflux. After 3 hours no ICEM could be detected by infrared analysis. The reaction mixture was then slowly added to 6 L of anhydrous ethyl ether and the solid collected. Precipitation of the PVP macromer was repeated, from ethanol into 4 L of ethyl ether. After drying at 30°C under reduced pressure the yield of macromer was 7.1 g (78%). The Mn (number average molecular weight) and Pd (polydispersity) values were 1,986 and 1.4 (vs. polyethylene glycol standards).

EXAMPLE 3

Copolymerization of OFPMA and PVP Macromer

1H,1H,5H Octafluoropentylmethacrylate, (OFPMA) 0.75 g, PVP macromer (Example 2), 5.0 g, 2-mercaptoethanol, 105 uL, and AIBN (recrystallized from ethanol), 8.2 mg, were combined with 100 mL of anhydrous tetrahhdrofuran (THF) in a 250 mL three neck flask. The flask was also fitted with a mechanical stirrer and a reflux condenser. A slow stream of nitrogen was used to deoxygenate the solution for 15 minutes. After 20 hours of reflux under a nitrogen

atmosphere the hydroxy terminated polymer was precipitated from 2 L of anhydrous ethyl ether. The solid was dissolved in 200 ml of THF and the precipitation repeated once. The white solid was dried under reduced pressure leaving 4.14 g, a 72% yield.

EXAMPLE 4

Polymerization of N,N-Dimethylacrylamide(DMA)

Distilled DMA, 20 g, 2-mercaptoethanol, 280 uL, and AIBN (recrystallized from ethanol), 0.33 g, were combined with 100 mL of anhydrous tetrahhyrofuran (THF) in a 250 mL three neck flask. The flask was also fitted with a mechanical stirrer and a reflux condenser. A slow stream of nitrogen was used to deoxygenate the solution for 15 minutes. After 20 hours of reflux under a nitrogen atmosphere no vinyl protons could be detected in the 60 Mhz NMR spectra (6.5-7.0 ppm). The hydroxy terminated polymer was precipitated from 2 L of anhydrous ethyl ether. The solid was dissolved in 100 ml of THF and the precipitation repeated. The white solid was dried under reduced pressure at 30°C. The yield was 15.5 g and the Mn (number average molecular weight), Mw (weight average molecular weight) and Pd (polydispersity) values were 6,700, 11,318 and 1.7 (vs. polyethylene glycol standards).

EXAMPLE 5

Preparation of a DMA Macromonomer

Hydroxy terminated copolymer, 12 g (from Example 4) was dissolved in 90 mL of chloroform, in a 250 mL 3-neck flask fitted with a magnetic stirrer and

a reflux condenser and an addition funnel. Dibutyltin dilaurate, 36.9 mg, and butylated hydroxy toluene (BHT), 10.2 mg, were added. Isocyanatoethyl methacrylate, 0.30 g (ICEM) in 10 mL $CHCl_3$, was added dropwise. Following the addition the solution was heated to reflux. After 48 hours no ICEM could be detected by infrared analysis. The reaction mixture was then slowly added to 2 L of anhydrous ethyl ether and the solid collected. The precipitation was repeated a second time followed by drying at 30°C under reduced pressure. The yield of macromer was 8.6 g. The Mn, Mw and Pd values were 4,400, 7,900 and 1.8 (vs. polyethylene glycol standards).

EXAMPLE 6

Copolymerization of OFPMA and DMA Macromer

OFPMA, 1.2 g, DMA macromer (Example 5), 6.7 g, 2-mercaptoethanol, 105 uL, and AIBN (recrystallized from ethanol), 8 mg, were combined with 100 mL of anhydrous tetrahhdrofuran (THF) in a 250 mL three-neck flask. The flask was also fitted with a magnetic stirrer and a reflux condenser. A slow stream of nitrogen was used to deoxygenate the solution for 15 minutes. After 72 hours of reflux under a nitrogen atmosphere the conversion to copolymer was 44%, (by NIR analysis). Addition of 25 mg AIBN and 48 hours refluxing, (120 hours total) gave a 60% conversion to copolymer. Precipitation into 2 L of anhydrous ethyl ether, followed by drying at reduced pressure left 6 g of copolymer with Mn, Mw, and Pd values of 4,600, 8,100, and 1.8 (vs. PEG standards).

EXAMPLES 7-10

Copolymerization of 1H,1H,5H Octafluoropentylmethacrylate and Methoxy polyethylene glycol monomethacrylates

Example 7

A solution was prepared by dissolving 9.1 g of methoxy polyethylene glycol 1,000 monomethacrylate in 100 mL of toluene. The solution was carefully transferred to a 250 mL three neck flask fitted with a magnetic stirrer and a condenser. To this, 9.1 g of 1H,1H,5H Octafluoropentylmethacrylate (OFPMA), 1.26 g of distilled thioglycolic acid (TGA) and 0.071 g of azobisisobutyronitrile (AIBN) were added. AIBN was recrystallized from ethanol before use. The solution was then deoxygenated using nitrogen for 15 minutes and then placed under a passive nitrogen blanket. After stirring for 16 hours at 60°C the percent conversion was determined to be 95-98% by near infrared (NIR) analysis. The number average molecular weight was determined by size exclusion chromatography ("SEC") vs. polystyrene and by end group titration. The Mn values were 2,902 and 1,815 respectively. Results are shown in Table I.

Examples 8-9

The procedure of Example 7 was repeated using higher relative amounts of methoxy polyethylene glycol 1000 monomethacrylate. THF replaced toluene as the solvent in Example 9. Results are shown in Table I.

Example 10

The procedure of Example 7 was repeated using methoxy polyethylene glycol 5000 monomethacrylate and using THF as the solvent. Results are shown in Table I.

Table I

ACID TERMINATED COPOLYMERS

Example #	Type	Composition	Solvent	Rxn time	Mn	Mw	Pd
7	OFPMA/Peo 1k	80/20	Toluene	16h	2902	5370	1.8
8	OFPMA/Peo 1k	70/30	Toluene	72h	2300	3400	1.44
9	OFPMA/Peo 1k	50/50	THF	24h	3163	5287	1.7
10	OFPMA/Peo 5k	80/20	THF	24h	12.6k	9400	1.34

EXAMPLE 11

Copolymerization of 3-Methacryloyloxypropyltris(trimethylsiloxy)silane and Methoxy polyethylene glycol 1,000 monomethacrylate

A solution was prepared by dissolving 7.1 g of methoxy polyethylene glycol 1,000 monomethacrylate in 100 ml of toluene. The solution was carefully transferred to a 250 ml three-neck flask fitted with a magnetic stirrer and a condenser. To this, 12.8 g of 3-methacryloyloxypropyltris(trimethylsiloxy)silane (TRIS), 1.0 g of distilled thioglycolic acid (TGA) and 0.059 g of azobisisobutyronitrile (AIBN) were added. AIBN was recrystallized from ethanol before use. The solution was then deoxygenated using nitrogen for 15 minutes and then placed under a passive nitrogen blanket. After stirring for 16 hours at 60°C the percent conversion was determined to be 95-98% by near infrared (NIR) analysis. The number average molecular weight was determined by size exclusion chromatography vs. polystyrene and by end group titration. The Mn values were 2,895 and 2,083 respectively. The polydispersity of the copolymer was 1.5.

EXAMPLES 12-17

Copolymerization of 1H,1H,5H Octafluoropentylmethacrylate and Methoxy polyethylene glycol monomethacrylates

Example 12

OFPMA, 15 g, methoxy polyethylene glycol 1,000 monomethacrylate, 50 g, 2-mercaptoethanol, 2.34 g, and

AIBN (recrystallized from ethanol), 0.164 g, were combined with 500 mL of a 1:1 mixture of THF and methanol(MEOH) in a 1 L, three-neck flask. The flask was also fitted with a magnetic stirrer and a reflux condenser. The mixture was stirred until all reagents were in solution. A slow stream of nitrogen was then used to deoxygenate the solution for 15 minutes. After 72 hours of reflux under a nitrogen atmosphere the conversion to copolymer was 99+% (by NIR analysis). Solvent was removed by flash evaporation leaving a viscous oil, which upon standing formed a wax-like solid. Values for Mn, Mw and Pd were determined vs. polystyrene, (Mn= 3,700, Mw= 6,300 and Pd= 1.72). Results are shown in Table II.

Examples 13-17

The procedure of Example 12 was repeated using methoxy polyethylene glycol monomethacrylate in different molecular weights and relative amounts as indicated in Table II which also summarizes the results obtained.

Table II

HYDROXY TERMINATED COPOLYMERS

Example #	Type	Composition	Conversion, time %(by NIR)	hrs	Mn	Mw	Pd
12	OFPMA/Peo 400	50/50	95	48	2190	3400	1.56
13	OFPMA/Peo 1k	50/50	99	72	3700	6300	1.72
14	OFPMA/Peo 5k	80/20	90	72	10.5k	16.1k	1.52
15	OFPMA/Peo 5k	50/50	75	65	10k	12.6k	1.27
16	OFPMA/Peo 2k	50/50	79	65	-	-	-
17	OFPMA/Peo 2k	80/20	95	48	3900	4800	1.22

EXAMPLES 18-21

Surface Active Macromonomer Preparation

Example 18

Distilled glycidyl methacrylate, 1.83 g, p-methoxyphenol, 2.5 mg (MEHQ), and two drops of N,N-dimethyldodecylamine were added to the solution from Example 7. The mixture was allowed to reflux under a nitrogen atmosphere for 5 hours. The solution was washed 3 times with dilute sodium carbonate solution and once with water. The organic layer was dried over magnesium sulfate, and toluene removed by flash evaporation at reduced pressure. The residue, 18.12 g (85% yield), of viscous yellow macromonomer had Mn values of 3,353 (by SEC vs. polystyrene) and 3,416 (by vapor phase osmometry,vpo). The polydispersity (Pd) of the macromonomer was 1.9. Results are summarized in Table III.

Examples 19-21

The procedure of Example 18 was repeated using the solutions from Examples 8-10. The copolymers of Examples 9-10 were isolated and redissolved in dioxane for surface active macromonomer preparation. Results obtained are shown in Table III.

Table III

SURFACE ACTIVE MACROMERS

Example #	Type	Composition	Solvent	Rxn time	Mn	Mn	Pd
18	OFPMA/Peo 1k	80/20	Toluene	5h	3353	6493	1.9
19	OFPMA/Peo 1k	70/30	Toluene	5h	2057	4587	2.2
20	OFPMA/Peo 1k	50/50	Dioxane	5h	2545	4351	1.7
21	OFPMA/Peo 5k	80/20	Dioxane	5h	8142	12k	1.5

EXAMPLES 22-27

Surface Active Macromonomer Preparation

Example 22

Hydroxy terminated copolymer, 41.744 g (from Example 12), was dissolved in 225 mL of THF, in a 500 mL 3-neck flask fitted with a magnetic stirrer, a reflux condenser, and an addition funnel. Dibutyltin dilaurate, 1.57 g, and butylated hydroxy toluene, 10 mg, were added. Isocyanatoethyl methacrylate, 1.98 g (ICEM) in 25 mL $CHCl_3$, was added dropwise. Following the addition the solution was heated to reflux. After 16 hours 0.2% ICEM was detected by infrared analysis. Methanol, 5 mL, was added to react with the slight excess of ICEM. Chloroform was then removed by flash evaporation. The residue was left under high vacuum overnight to remove residual solvent leaving 42.4 g of wax-like semisolid. Values for the Mn, Mw, and Pd were determined vs polystyrene standards. Results are summarized in Table IV.

Examples 23-27

The procedure of Example 22 was repeated using hydroxy terminated copolymers (dissolved in chloroform) from Examples 13-17. Results are shown in Table IV.

Table IV

SURFACE ACTIVE MACROMERS

Example #	Type	Composition	Solvent	Time hrs	Mn	Mn	Pd
22	OFPMA/Peo 400	50/50	THF	16	2500	4600	1.8
23	OFPMA/Peo 1k	50/50	$CHCl_3$	16	4000	6700	1.69
24	OFPMA/Peo 5k	80/20	$CHCl_3$	12	4100	4500	1.12
25	OFPMA/Peo 5k	50/50	$CHCl_3$	16	9900	12.5K	1.26
26	OFPMA/Peo 2k	50/50	$CHCl_3$	16	-	-	-
27	OFPMA/Peo 2k	80/20	$CHCl_3$	16	3800	4500	1.19

EXAMPLE 28

Surface Active Macromonomer Preparation

Distilled glycidyl methacrylate, 1.58 g, p-methoxyphenol, 2.8 mg (MEHQ), and two drops of N,N-dimethyldodecylamine were added to the solution from Example 11. The mixture was allowed to reflux under a nitrogen atmosphere for 5 hours. The solution was washed 3 times with dilute sodium carbonate solution and once with water. The organic layer was dried over magnesium sulfate, and toluene was removed by flash evaporation at reduced pressure. The residue, 17.64 g (84% yield), of viscous semi-solid macromonomer had Mn values of 1,593 (by SEC vs. polystyrene) and 1,918 (by vapor phase osmometry,vpo). The polydispersity of the macromonomer was 1.6.

EXAMPLE 29

Surface Active Macromonomer Preparation

Hydroxy terminated copolymer, 3.14 g (from Example 3), was dissolved in 90 mL of chloroform, in a 250 mL 3-neck flask fitted with a magnetic stirrer, a reflux condenser, and an addition funnel. Dibutyltin dilaurate, 3 drops and butylated hydroxy toluene, 3 mg, were added. Isocyanatoethyl methacrylate, 89 uL (ICEM) in 10 mL $CHCl_3$, was added dropwise. Following the addition the solution was heated to reflux. After 12.5 hours no ICEM could be detected by infrared analysis. The reaction mixture was then slowly added to 2 L of anhydrous ethyl ether and the solid collected. After drying at 30°C under reduced pressure

the yield of macromer was 3 g. The Mn, Mw and Pd values were 4,900, 5,900 and 1.2 (vs. polyethylene glycol standards).

EXAMPLE 30

Surface Active Macromonomer Preparation

Hydroxy terminated copolymer, 4.5 g, (from Example 6) was dissolved in 90 mL of chloroform in a 250 mL 3-neck flask fitted with a magnetic stirrer, a reflux condenser, and an addition funnel. Dibutyltin dilaurate, 2 drops and butylated hydroxy toluene, 3 mg, were added. Isocyanatoethyl methacrylate, 93 uL (ICEM) in 10 mL $CHCl_3$, was added dropwise. Following the addition the solution was heated to reflux. After 20 hours a trace of ICEM could be detected by infrared analysis. The reaction mixture was then slowly added to 2 L of anhydrous ethyl ether and the solid collected. After drying at 30°C under reduced pressure the yield of macromer was 3.14 g. The Mn, Mw and Pd values were 4,900, 8,900 and 1.8 (vs. PEG standards).

EXAMPLES 31-42

Surface Tension Determination Using the Wilhelmy Plate Technique

Macromonomer solutions were prepared with distilled water at molar concentrations of 10^{-2}-10^{-6}. The surface tension of each solution was measured by the Wilhelmy Plate technique on a Wettek, model SFA-212, instrument. A test solution was placed in a jacketed beaker, which had been cleaned with chromic/sulfuric acid for 40 minutes, rinsed with clean water and dried overnite at 120°C. Data was collected by dipping a glass cover slip (cleaned by passing through a flame) into each solution several times at the following conditions:

Platform speed	0.16 mm/sec
Immersion depth	20.0 mm
Temperature	34 ± 1°C

The data was analyzed using WETTEK 12 software. Results are shown below in Table V.

Table V

SURFACE TENSION DATA

Example #	Macromer example #	Molar conc.	Temp. #C	Surface Tension dyne/cm
31	7	10^{-2}	34	32.3
32	7	10^{-3}	34	34.8
33	7	10^{-4}	34	46.8
34	5	10^{-3}	23	36.3
35	5	10^{-4}	23	46.2
36	5	10^{-5}	23	57.5
37	5	10^{-6}	23	66.8
38	6	10^{-2}	23	31.8
39	6	10^{-3}	23	34.3
40	6	10^{-4}	23	38.7
41	6	10^{-5}	23	53.1
42	6	10^{-6}	23	65.9

EXAMPLE 43

Polyurethane Monomer Mix

A urethane prepolymer prepared from isophorone diisocyanate, diethylene glycol, polysiloxanediol (molecular wt. 3,000) and endcapped with 2-hydroxyethyl methacrylate was combined with the following; methacryloyloxypropyl tris(trimethylsiloxy)silane (TRIS), N,N-dimethylacrylamide (DMA), N-hexanol, benzoin methyl ether (BME). The proportions are given below.

Urethane prepolymer	35 parts
TRIS	35 parts
DMA	30 parts
N-hexanol	40 parts
BME	0.2 parts

The resulting clear mix was then filtered through a 1.2 micron filter into a clean glass vial.

EXAMPLE 44

Contact Lens Cast Molding

Anterior and posterior mold surfaces were cleaned by electrostatic deionization in air and transferred to an inert (nitrogen) atmosphere. The mold anterior was then filled with 40-80 uL of monomer mix, (Example 43) in the inert atmosphere and placed on a casting plate. The mold posterior was then positioned. Once the casting plate was full the top plate was aligned and tightened down to 18 inch-pounds. Casting plates were

then placed under ultraviolet light at 4,000 u watts/cm^2,(oxygen level was <50ppm), for one hour. Following separation the mold halves containing lenses were placed in a 70/30 volume by volume solution of ethanol and water or 100% ethanol. Lenses and solution were placed in an ultrasonic bath at 50°C and allowed to release. Lenses were then transferred to absolute ethanol. After one hour the solvent was exchanged with fresh ethanol and allowed to stand for 48 hours. Ethanol was then removed by water extraction.

EXAMPLE 45

Surface Coating of Polyurethane Contact Lenses

A solution of 0.1 mmol surface-active macromer of Example 18, 0.007 g of neopentyl glycol dimethacrylate, and 0.0038 g of BME in 100 mL of deoxygenated, distilled water was prepared by stirring at room temperature for one hour. One contact lens prepared as described in Example 44 was placed in a 10 mL lens vial and the vial was filled with the solution under a nitrogen atmosphere in a glove box. The vial was sealed with a Teflon lined stopper and crimp seal, placed on its side and irradiated with 2500 uW/cm^2 of UV light for 2 hours. The lens was removed from the vial, washed with distilled water, extracted in ethanol for 2 hours and boiled in distilled water for 2.5 hours. The lens was then sealed in a vial in buffered saline solution.

EXAMPLE 46

Surface Coating of Polyurethane Contact Lenses

A solution of 0.1 mmol surface-active macromer of Example 20, 0.01 g of neopentyl glycol dimethacrylate and 0.003 g of BME in 100 mL of deoxygenated, distilled water was prepared by stirring at room temperature for one hour. One contact lens prepared as described in Example 44 was placed in a 10 mL lens vial and the vial was filled with the solution under a nitrogen atmosphere in a glove box. The vial was sealed with a Teflon lined stopper and crimp seal, placed on its side and irradiated with 2500 uW/cm^2 of UV light for 2 hours. The lens was removed from the vial, washed with distilled water, extracted in ethanol for 2 hours and boiled in distilled water for 2.5 hours. The lens was then sealed in a vial in buffered saline solution.

EXAMPLE 47

Surface Coating of Silicone (SIL-TECH) Contact Lenses

A solution of 0.1 mmol surface-active macromer of Example 18, 0.007 g of neopentyl glycol dimethacrylate, and 0.003 g of BME in 100 mL of deoxygenated, distilled water was prepared by stirring at room temperature for one hour. A SiL-TECH silicone elastomer contact lens (available from Bausch & Lomb Incorporated) was placed in a 10 mL lens vial and the vial was filled with the solution under a nitrogen atmosphere in a glove box. The vial was sealed with a Teflon lined stopper and crimp seal, placed on its side and irradiated with 2500 uW/cm^2 of UV light for 2 hours. The lens was removed from the vial, washed with distilled water,

extracted in 1:1 ethanol:isopropanol for 3 hours. The lens was then sealed in a vial in buffered saline solution.

EXAMPLE 48

Analysis for Surface-Active Macromer at Contact Lens Surface

Contact Angle

The contact angle of the surface coated lenses of Example 47 was measured and compared to an untreated lens (control). The average contact angle of three coated lenses was 38° versus 46° for the control sample.

EXAMPLE 49

Clinical Evaluation

Five subjects wore one contact lens of Example 45 and one control contact lens (the uncoated lens of Example 44) in the other eye. The lenses were analyzed after one hour of wear for surface characteristics of wettability and surface deposition. The wettability rating scale was 0-4, where 0 was more than 2/3 of the anterior lens surface unwetted by tear film and 4 represented complete (100%) wetting by tear film. The deposition scale was 0-4 where 0 represented no surface deposits and 4 was multiple deposits of 0.5mm diameter or larger. The results were wettability 2.8 and deposits 1.2 which compares favorably to values of 1.0 and 1.8, respectively for wettability and deposits for uncoated control lenses of Example 44.

What is claimed is:

1. A method of modifying the surface of a polymeric object which comprises immersing the polymeric object in an aqueous dispersion of a polymerizable surfactant, a cross-linking agent, and a free radical initiator and exposing the immersant to ultraviolet light to form a permanent, cross-linked surface coating on the object.

2. The method of claim 1 wherein the polymerizable surfactant is a surface active macromer described by the formula:

$$DC[A_xB_y]$$

wherein A is at least one ethylenically unsaturated hydrophilic monomer, B is at least one ethylenically unsaturated hydrophobic monomer, C is a functional chain transfer agent, D is an ethylenically unsaturated end group, y is within the range from about 0.1 to about 0.9, and $x + y = 1$.

3. The method of claim 2 wherein A is selected from the group consisting of ethylenically unsaturated polyoxyalkylenes, polyacrylamides, polyvinylpyrrolidones, polyvinyl alcohols, poly (HEMA), and N-alkyl-N-vinyl acetamide.

4. The method of claim 2 wherein A is an ethylenically unsaturated polyoxyalkylene selected from the group consisting of (meth)acrylated polyoxyalkylenes, (meth)acrylamido polyoxyalkylenes, styrenyl polyoxyalkylenes, alkenyl polyoxyalkylenes,

vinyl carbonate polyoxyalkylenes and vinyl carbamate polyoxyalkylenes.

5. The method of claim 4 wherein the polyoxyalkylene is polyethylene oxide.

6. The method of claim 2 wherein A is (meth)acrylated polyethylene oxide.

7. The method of claim 6 wherein A is methoxy polyethylene glycol methacrylate.

8. The method of claim 3 wherein A is a methacrylate endcapped poly-N-vinylpyrrolidinone.

9. The method of claim 3 wherein A is a methacrylate endcapped poly-N,N-dimethylacrylamide.

10. The method of claim 2 wherein B is selected from the group consisting of alkyl (meth)acrylates, N-alkyl (meth)acrylamides, alkyl vinylcarbonates, alkyl vinylcarbamates, fluoroalkyl (meth)acrylates, N-fluoroalkyl (meth)acrylamides, N-fluoroalkyl vinylcarbonates, N-fluoroalkyl vinylcarbamates, silicone-containing (meth)acrylates, (meth)acrylamides, vinyl carbonates, vinyl carbamates, styrenic monomers and polyoxypropylene (meth)acrylates.

11. The of claim 10 wherein the styrenic monomers are selected from the group consisting of styrene, alpha-methyl styrene, para-methyl styrene, para-t-butyl monochloro styrene, and para-t-butyl dichloro styrene.

12. The method of claim 10 wherein B is 1-H,1-H,5-H-octafluoropentyl methacrylate.

13. The method of claim 2 wherein C is selected from the group consisting of mercapto carboxylic acids, mercapto alcohols, and aminomercaptans.

14. The method of claim 13 wherein C is thioglycolic acid.

15. The method of claim 13 wherein C is 2-mercaptoethanol.

16. The method of claim 13 wherein C is 2-aminoethane thiol.

17. The method of claim 14 wherein D is a (meth)acrylated hydroxy ester moiety derived from glycidyl (meth)acrylate.

18. The method of claim 15 wherein D is a (meth)acrylated ester moiety derived from (meth)acryloyl chloride.

19. The method of claim 15 wherein D is a (meth)acrylated urethane moiety derived from (meth)acrylated isocyanate.

20. The method of claim 16 wherein D is a (meth)acrylated urea moiety derived from (meth)acrylated isocyanate.

21. The method of claim 15 wherein D is a vinylcarbonate moiety derived from vinyl chloroformate.

22. The method of claim 16 wherein D is a (meth)acrylated amide moiety derived from (meth)acryloyl chloride.

23. The method of claim 16 wherein D is a vinylcarbamate moiety derived from vinyl chloroformate.

24. The method of claim 1 wherein the polymeric object is a contact lens.

25. The method of claim 24 wherein the contact lens is a hydrogel contact lens.

26. The method of claim 24 wherein the contact lens is a rigid gas permeable lens.

27. The method of claim 24 wherein the contact lens is a silicone elastomer contact lens.

28. The method of claim 1 wherein the cross-linking agent is selected from the group consisting of hydrophobic molecules having two or more polymerizable groups.

29. The method of claim 28 wherein the cross-linking agent is selected from the group consisting of hydrophobic molecules having two or more (meth)acrylate groups.

30. The method of claim 28 wherein the cross-linking agent is selected from the group consisting of hydrophobic molecules having two or more (meth)acrylamide groups.

31. The method of claim 28 wherein the cross-linking agent is neopentyl glycol dimethacrylate.

32. The method of claim 1 wherein the aqueous dispersion contains a polymerizable surfactant at a molar concentration of about 0.1 to 0.0001, from about 1 to about 10^{-4} parts by weight of a cross-linking agent, and from about 0.1 to about 10^{-4} parts by weight of a free radical initiator.

33. A surface-modified polymeric object prepared by immersing the object in an aqueous dispersion of a polymerizable surfactant, a cross-linking agent, and a free radical initiator and exposing the immersant to ultraviolet light to form a permanent, cross-linked surface coating on the object.

34. The surface-modified polymeric object of claim 33 wherein the object is a contact lens.

AMENDED CLAIMS

[received by the International Bureau on 25 May 1992 (25.05.92) ; original claims 1-34 replaced by amended claims 1-34 (4 pages)]

1. A method of modifying the surface of a polymeric object which comprises immersing the polymeric object in an aqueous dispersion of a surface active macromer described by the formula: DC $[A_xB_y]$ wherein A is at least one ethylenically unsaturated hydrophobic monomer, B is at least one ethylenically unsaturated hydrophilic monomer, C is a functional claim transfer agent, D is an ethylenically unsaturated end group, y is within the range from about 0.1 to about 0.9, and x+y = 1, a hydrophobic cross-linking agent, and a free radical initiator and exposing the immersed polymeric object to ultraviolet light to form a permanent, cross-linked surface coating on the polymeric object.

3. The method of claim 1 wherein A is selected from the group consisting of ethylenically unsaturated polyoxyalkylenes, polyacrylamides, polyvinylpyrrolidones, polyvinyl alcohols, poly (HEMA), and N-alkyl-N-vinyl acetamide.

4. The method of claim 1 wherein A is an ethylenically unsaturated polyoxyalkylene selected from the group consisting of (meth)acrylated polyoxyalkylenes, (meth)acrylamido polyoxyalkylenes, styrenyl polyoxyalkylenes, alkenyl polyoxyalkylenes, vinyl carbonate polyoxyalkylenes and vinyl carbamate polyoxyalkylenes.

5. The method of claim 4 wherein the polyoxyalkylene is polyethylene oxide.

6. The method of claim 1 wherein A is (meth)acrylated polyethylene oxide.

7. The method of claim 6 wherein A is methoxy polyethylene glycol methacrylate.

8. The method of claim 3 wherein A is a methacrylate endcapped poly-N-vinylpyrrolidinone.

9. The method of claim 3 wherein A is a methacrylate endcapped poly-N,N-dimethylacrylamide.

10. The method of claim 1 wherein B is selected from the group consisting of alkyl (meth)acrylates, N-alkyl (meth)acrylamides, alkyl vinylcarbonates, alkyl vinylcarbamates, fluoroalkyl (meth)acrylates, N-fluoroalkyl (meth)acrylamides, N-fluoroalkyl vinylcarbonates, N-fluoroalkyl vinylcarbamates, silicone-containing (meth)acrylates, (meth)acrylamides, vinyl carbonates, vinyl carbamates, styrenic monomers and polyoxypropylene (meth)acrylates.

11. The method of claim 10 wherein the styrenic monomers are selected from the group consisting of styrene, alpha-methyl styrene, para-methyl styrene, para-t-butyl monochloro styrene, and para-t-butyl dichloro styrene.

12. The method of claim 10 wherein B is 1-H,1-H,5-H-octafluoropentyl methacrylate.

13. The method of claim 1 wherein C is selected from the group consisting of mercapto carboxylic acids, mercapto alcohols, and aminomercaptans.

14. The method of claim 13 wherein C is thioglycolic acid.

15. The method of claim 13 wherein C is 2-mercaptoethanol.

16. The method of claim 13 wherein C is 2-aminoethane thiol.

17. The method of claim 14 wherein D is a (meth)acrylated hydroxy ester moiety derived from glycidyl (meth)acrylate.

18. The method of claim 15 wherein D is a (meth)acrylated ester moiety derived from (meth)acryloyl chloride.

19. The method of claim 15 wherein D is a (meth)acrylated urethane moiety derived from (meth)acrylated isocyanate.

20. The method of claim 16 wherein D is a (meth)acrylated urea moiety derived from (meth)acrylated isocyanate.

21. The method of claim 15 wherein D is a vinylcarbonate moiety derived from vinyl chloroformate.

22. The method of claim 16 wherein D is a (meth)acrylated amide moiety derived from (meth)acryloyl chloride.

23. The method of claim 16 wherein D is a vinylcarbamate moiety derived from vinyl chloroformate.

24. The method of claim 1 wherein the polymeric object is a contact lens.

25. The method of claim 24 wherein the contact lens is a hydrogel contact lens.

26. The method of claim 24 wherein the contact lens is a rigid gas permeable lens.

27. The method of claim 24 wherein the contact lens is a silicone elastomer contact lens.

28. The method of claim 1 wherein the cross-linking agent is selected from the group consisting of hydrophobic molecules having two or more polymerizable groups.

29. The method of claim 28 wherein the cross-linking agent is selected from the group consisting of hydrophobic molecules having two or more (meth)acrylate groups.

30. The method of claim 28 wherein the cross-linking agent is selected from the group consisting of hydrophobic molecules having two or more (meth)acrylamide groups.

31. The method of claim 28 wherein the cross-linking agent is neopentyl glycol dimethacrylate.

32. The method of claim 1 wherein the aqueous dispersion contains a surface active macromer at a molar concentration of about 0.1 to 0.0001, from about 1 to about 10^{-4} parts by weight of a cross-linking agent, and from about 0.1 to about 10^{-4} parts by weight of a free radical initiator.

33. A surface-modified polymeric object prepared by immersing the polymeric object in an aqueous dispersion of a surface active macromer described by the formula: DC $[A_xB_y]$ wherein A is at least one ethylenically unsaturated hydrophobic monomer, B is at least one ethylenically unsaturated hydrophilic monomer, C is a functional claim transfer agent, D is an ethylenically unsaturated end group, y is within the range from about 0.1 to about 0.9, and x+y = 1, a hydrophobic cross-linking agent, and a free radical initiator and exposing the immersed polymeric object to ultraviolet light to form a permanent, cross-linked surface coating on the polymeric object.

34. The surface-modified polymeric object of claim 33 wherein the object is a contact lens.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/08729

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08J7/04; C08F299/00; G02B1/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08J ; C08F ; G02B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
A	EP,A,0 352 199 (TERUMO KABUSHIKI KAISHA) 24 January 1990 see claims 1-7	1
A,P	EP,A,0 424 873 (TOSOH CORPORATION) 2 May 1991 see claims 1-7	1
A	EP,A,0 293 963 (DOW CHEMICAL COMPANY) 7 December 1988 see claims 1,8-10 see page 2, line 37 - line 50 see page 11, line 33 - line 37	1
A	US,A,4 900 627 (JEFFREY H. HARWELL) 13 February 1990 see claim 1 see column 1, line 38 - line 64 see column 2, line 63 - column 3, line 2	1

-/--

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28 APRIL 1992	06. 05. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DEPIJPER R.D.C.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 378 512 (CIBA-GEIGY AG.) 18 July 1990 see claims 1,8,9,12,20,21 see page 3, line 54 - page 4, line 19 see page 6, line 13 - page 7, line 57	1
A	US,A,4 910 268 (SHIRO KOBAYASHI) 20 March 1990 see claims 1,5 see column 1, line 13 - line 23 see column 5, line 11 - line 16 see column 5, line 42 - line 53	1
A	US,A,4 929 510 (ELI RUCKENSTEIN) 29 May 1990 see claims 1-6	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9108729 SA 55175

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/04/92
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